

# PATENT ABSTRACTS OF JAPAN

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## (54) PRODUCTION OF CARBON OF MOLECULAR SIEVE

### (57)Abstract:

PURPOSE: To obtain high-performance molecular sieve carbon having excellent equilibrium separation type molecular sieve to methane, etc., by heating optically isotropic pitch in an inert gas containing an aromatic hydrocarbon, etc., and depositing thermally decomposed carbon on microholes of a porous carbon base material in a given condition.

CONSTITUTION: Optically isotropic pitch having  $\geq 150^{\circ}\text{C}$  softening temperature and  $\leq 5,000\text{ppm}$  ash content is infusibilized, activated in an inert gas atmosphere containing a carbon dioxide gas and/or steam to give porous carbon (carbonaceous base material) having 300-1,000 specific surface area. Then in a treating furnace heated to  $650-850^{\circ}\text{C}$ , an inert gas containing an aromatic hydrocarbon and/or an alicyclic hydrocarbon is supplied to the carbon base material having 5.5-12A average micropore diameter and thermally decomposed carbon is deposited on the micropores. After the completion of the deposition treatment, the carbon base material is successively maintained in an inert gas atmosphere at the deposition temperature to  $1,100^{\circ}\text{C}$ .

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CLAIMS

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[Claim(s)]

[Claim 1] The manufacture approach of the molecular sieve carbon characterized by supplying the inert gas containing aromatic hydrocarbon and/or alicyclic hydrocarbon, and vapor-depositing pyrolytic carbon to micropore all over the processing furnace which heated the carbonaceous base material which has a 5.5-12A diameter of average micropore at 650-850 degrees C.

[Claim 2] The manufacture approach of the molecular sieve carbon characterized by supplying the inert gas containing aromatic hydrocarbon and/or alicyclic hydrocarbon to this fission reactor, and carrying out vacuum evaporation processing all over the processing furnace which was heated by 650-850 degrees C under the inert gas ambient atmosphere, and was heated by 650-850 degrees C in the carbonaceous base material which has a 5.5-12A diameter of average micropore.

[Claim 3] The manufacture approach of molecular sieve carbon according to claim 1 or 2 that said carbonaceous base material is characterized by manufacturing 150 degrees C or more of softening temperatures, and the optical-isotropy pitch of 5000 ppm or less of ash content as a raw material.

[Claim 4] claims 1-3 which subsequently cast, perform activation processing under the inert gas ambient atmosphere which contains carbon dioxide gas and/or a steam further, consider [ 150 degrees C or more of softening temperatures and the optical-isotropy pitch of 5000 ppm or less of ash content are made into grinding or fiber, and non-deliquest / of this / is carried out, and ] as the porous carbon of specific surface area of 300-1000m<sup>2</sup> / g, and use this as said carbonaceous base material -- the manufacture approach of molecular sieve carbon given in either.

[Claim 5] claims 1-4 characterized by holding at the temperature of 1100 degrees C or less beyond vacuum evaporation processing temperature under an inert gas ambient atmosphere succeeding after said vacuum evaporation processing termination -- the manufacture approach of molecular sieve carbon given in either.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of the molecular sieve carbon used for gas separation technology, such as separation of the methane out of the hydrogen purification from the air separation by the PSA technique, off-gas, etc., and fermentation gas.

[0002]

[Description of the Prior Art] In recent years, the ED which separates a specific component and is refined is prosperous out of [ various ] mixed gas. The technique called PSA especially has compact equipment, and since the running cost is low, the expansion to many applications is expected. Especially as for the air separation which uses hydrophobic molecular sieve carbon, and separates and collects nitrogen from air, it counts upon a rapid commercial-scene expansion with increase of nitrogen need. The description of molecular sieve carbon is to usual activated carbon having 10-30A micropore to have the micropore of small and narrow distribution of 3-5A. Although various approaches are proposed about the manufacture approach of molecular sieve carbon, pyrolytic carbon vacuum deposition is in it.

[0003] This pyrolytic carbon vacuum deposition contacts a carbonaceous base material and hydrocarbon gas at an elevated temperature, it is making the pyrolytic carbon emitted from a hydrocarbon vapor-deposit near the entry of the micropore of a carbonaceous base material, and is an approach of adjusting the micropore of a carbonaceous base material, and has various kinds of proposals about this approach from before.

[0004] In a JP,52-18675,B specification the hydrocarbon (for example, benzene --) which emits carbon by the pyrolysis, using corks with few volatile components as a carbonaceous base material Toluene, ethane, a hexane, a methanol, etc. are added. At the temperature of 600-900 degrees C by [ for 1 - 60 minutes, or beyond it ] carrying out time amount processing By carrying out the deposition of the emitted carbon into the pore of this course, the process of the carbon content molecular sieve used for separation of gas with the small molecular dimension of about 4A or less is proposed.

[0005] Although this proposal is epoch-making and is evaluated in that the process of the carbon molecular sieve for separating a small molecule was begun and proposed, in order to obtain the carbon molecular sieve of the high quality which was excellent with sufficient repeatability, the further improvement is required for it.

[0006] Moreover, it sets on the Patent Publication Heisei No. 502743 [ one to ] specifications. It introduces all over the oscillating furnace to which the inert gas which has few dry distillation objects of a volatile component at the temperature of 800-900 degrees C, and has the steam concentration of 20 - 95 capacity % by the counterflow for 5 - 30 minutes is supplied. After being activated weakly, by introducing into the oscillating furnace to which the inert gas which has the benzene concentration of 5 - 12 capacity % by the counterflow is supplied, it excels in the separability of oxygen and nitrogen, and the manufacture approach of a molecular sieve of having uniform quality is indicated.

[0007] Although this proposal is excellent in the point that the product of more uniform quality is obtained, since it is the method which contacts by the counterflow, a process becomes complicated a little and the thing of high quality may not be obtained depending on the dry distillation object to be

used.

[0008] The process which carries out degasifying of the carbon base material at the (i) elevated temperature (800-900 degrees C) in a JP,60-171212,A specification as another proposal, (ii) The carbon base material after degasifying is cooled to the temperature of 300-500 degrees C. The process which makes the hydrocarbon of a gaseous phase contact and makes this hydrocarbon stick to the interior, (iii) The process which the hydrocarbon which fixed to the pore of the process and (iv) carbon base material from which the hydrocarbon which carried out degasifying to the bottom of reduced pressure of the carbon base material after adsorption, and was held physically is removed is disassembled [ process ] at an elevated temperature (800-900 degrees C), and carries out the deposition of the carbon to pore, The process of the molecular sieve carbon which consists of combination of the process of (i) - (iv) above is proposed. It indicates about the case where a propylene is used as a hydrocarbon by which a carbon base material is adsorbed, and it is supposed that it is most suitable for processing of a carbon base material in which it has 0.5-0.55nm (5-5.5A) pore, from the minimum dimension of a propylene.

[0009] According to this proposal, the molecular sieve carbon by which pyrolytic carbon carried out deposition only to opening of a carbon base material, and pore structure was controlled can be manufactured, but a production process becomes complicated and complicated as a whole.

[0010]

[Problem(s) to be Solved by the Invention] This invention aims at offer of the manufacture approach by which the molecular sieve carbon by such pyrolytic carbon vacuum deposition has been improved. More specifically, it aims at offer of the approach of manufacturing the molecular sieve carbon of high performance with sufficient repeatability cheaply simple.

[0011]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for the ability of the molecular sieve carbon of high performance to be manufactured with sufficient repeatability in a very simple process, when aromatic hydrocarbon or alicyclic hydrocarbon was used as a hydrocarbon using the place which took lessons from the relation between the diameter of micropore of a carbonaceous base material, and the class of hydrocarbon which is the generation source of pyrolytic carbon by having used the pitch as the start raw material, and inquired wholeheartedly, and the carbonaceous base material whose diameter of average micropore is 5.5-12A.

[0012] That is, according to the comprehensive concept of this invention, the manufacture approach of the molecular sieve carbon characterized by supplying the inert gas containing aromatic hydrocarbon and/or alicyclic hydrocarbon, and vapor-depositing pyrolytic carbon to micropore all over the processing furnace which heated the carbonaceous base material which has a 5.5-12A diameter of average micropore at 650-850 degrees C is offered.

[0013] Moreover, the manufacture approach of the molecular sieve carbon characterized by supplying the inert gas containing aromatic hydrocarbon and/or alicyclic hydrocarbon to this fission reactor, and carrying out vacuum evaporatio processing all over the processing furnace which was heated by 650-850 degrees C under the inert gas ambient atmosphere, and was heated by 650-850 degrees C in the carbonaceous base material which has a 5.5-12A diameter of average micropore is offered.

[0014] Said carbonaceous base material is manufactured here considering 150 degrees C or more of softening temperatures, and the optical-isotropy pitch of 5000 ppm or less of ash content as a raw material. 150 degrees C or more of softening temperatures, and the optical-isotropy pitch of 5000 ppm or less of ash content It is desirable to cast subsequently, to perform activation processing under the inert gas ambient atmosphere which contains carbon dioxide gas and/or a steam further, to consider [ consider as grinding or fiber, carry out non-deliquesce / of this / , ] as the porous carbon of specific surface area of 300-1000m<sup>2</sup> / g, and to use this as said carbonaceous base material.

[0015] Furthermore, it is desirable after said vacuum evaporatio processing termination to hold at the temperature of 1100 degrees C or less beyond vacuum evaporatio processing temperature under an inert gas ambient atmosphere succeedingly.

[0016]

[Elements of the Invention] Hereafter, although the configuration of this invention is explained in

full detail, the advantage based on a more desirable mode and more desirable it will become clear naturally.

[0017] The range of the diameter of average micropore of the carbonaceous base material used by carbonaceous base material this invention is 5.5-12A, and it is 5.5-8A 5.5-9A especially preferably. Distribution of the diameter of micropore of the molecular sieve carbon which will be obtained if distribution of the diameter of micropore of a carbonaceous base material is narrow also becomes narrow, and a suitable result is obtained. Since the rate (aging of the diameter of micropore) to which the diameter of micropore becomes narrow is too early in case vacuum evaporation processing is carried out with the carbon generated by the pyrolysis of aromatic hydrocarbon, when the diameter of average micropore is less than 5.5A carbonaceous base material, it becomes [ control of the path of micropore ] difficult and is not suitable. Moreover, since the micropore itself will become easy to be blocked in the case of vacuum evaporation processing if a pitch diameter exceeds 12A, it is not suitable.

[0018] In addition, the micropore in this invention shows pore 20A or less. Moreover, the diameter of average micropore means 50% pitch diameter of the micropore volume in the distribution curve of the diameter of micropore. The carbonaceous base material which has a diameter of average micropore within the limits of 5.5-12A can be obtained very easily according to the approach of explaining in full detail below by using the pitch of a coal system or a petroleum system as a start raw material.

[0019] Hereafter, the acquisition approach of a carbonaceous base material is described. 150 degrees C or more of softening temperatures are 150-250 degrees C preferably, and ash content grinds mechanically 5000 ppm or less and the desirable pitch of isotropy [ target / 500 ppm or less / optical ], and considers as the shape of fines. Or an isotropic pitch is heated optically and suppose that it is fibrous by the technique of melt spinning.

[0020] In order that non-deliquesce may take great time amount to softening temperature, it is not suitable for the pitch of 150 degrees C or less as a start raw material. Moreover, ash content makes the activation reaction later mentioned in order that ash content may act as a catalyst overrun recklessly, or the diameter of average micropore of the carbonaceous base material obtained is not [ that it is easy to exceed 12A ] suitable for the pitch of 5000 ppm or more as a start raw material from the point of \*\*. Under oxidizing atmospheres, such as air, to 300 degrees C, the temperature up of this fines-like pitch or fibrous pitch is carried out, and it carries out non-deliquesce.

[0021] It mixes with a binder and the fines-like object or fibrous object which carried out non-deliquesce is cast. It has the function to hold the configuration which was made to combine a fines-like object or fibrous objects, and was cast, and the pitch whose softening temperature is about 80-120 degrees C, phenol resin, furan resin, an epoxy resin, etc. can be illustrated as a binder here. Below 30 weight sections of the operating rate of a binder are desirable more than 2 weight sections to the fines-like object and fibrous object 100 weight section which carried out non-deliquesce as the carbon residue. When larger than 30 weight sections, activation processing becomes less easy and pore distribution becomes less as desirable as the raw material of breadth molecular sieve carbon. The effectiveness as a binder of the case above of under 2 weight sections is not discovered.

[0022] A non-deliquesce fines-like object is cast granular by the piston granulation method or the rolling corning method by this molding process. A fibrous non-deliquesce object is cast granular like a fines-like case, and, in addition to this, is cast by the paper by the wet paper-making method, the felt by the needle punch method, etc.

[0023] This cast is given to activation processing next. In activation processing, the carbon crystalline which constitutes charcoal material (activation raw material), or the carbon which constitutes a detailed porous space part carries out reaction consumption, porous space forms systematically intricately according to carbon structure, and specific surface area increases.

[0024] Activation processing is 800-1100 degrees C in temperature under inert gas ambient atmospheres, such as nitrogen gas containing the bottom of a carbon-dioxide-gas ambient atmosphere or carbon dioxide gas, or/and a steam, and is performed by leaving it for 0 to 480 minutes. Carbonization processing may be beforehand carried out at the temperature of 500-1500 degrees C in inert gas ambient atmospheres, such as nitrogen gas, before activation processing.

[0025] The diameter of average micropore can manufacture easily the carbonaceous base material in

within the limits which is 5.5-12A by controlling processing temperature and time amount by this activation processing so that the specific surface area of a processing object is set to 300-1000m<sup>2</sup> / g. of this level -- activation -- if it is-izing, activation yield (activation processing object weight to the molding weight of a fines-like object or a fibrous object comparatively) can obtain molecular sieve carbon cheaply highly with 50 - 70%.

[0026] Aromatic hydrocarbon or alicyclic hydrocarbon is used as a hydrocarbon used as the carbon source of the pyrolytic carbon vacuum deposition of hydrocarbon this invention. As aromatic hydrocarbon, although a cyclohexane etc. can be illustrated as alicyclic hydrocarbon, such as alkylbenzenes, such as benzene, toluene, ethylbenzene, and a xylene, other naphthalene, and a methylnaphthalene, that whose ring is generally 1 - 2 ring extent is desirable.

[0027] In vacuum evaporatio approach this invention, the 650-850 degrees C of the above-mentioned carbonaceous base materials are first heated to 700-800 degrees C preferably under an inert gas ambient atmosphere. This heating may be performed all over the processing furnace mentioned later, it may heat all over another furnace and the heated carbonaceous base material may be continuously supplied to a processing furnace.

[0028] 650-850 degrees C of vacuum evaporatio processings are preferably performed all over the processing furnace heated by 700-750 degrees C. All over a processing furnace, the carbonaceous base material with which the above was heated exists, and the inert gas represented with 0.1 to 20 capacity % and the nitrogen gas made desirable 3-10 capacity % content in aromatic hydrocarbon or alicyclic hydrocarbon is supplied there.

[0029] In addition, at less than 650 degrees C, there are few yields of pyrolytic carbon, vacuum evaporatio takes huge time amount, at the temperature exceeding 850 degrees C, the rate to which there are too many yields of pyrolytic carbon, and the diameter of micropore becomes narrow becomes quick, and the temperature of a processing furnace becomes out of control.

[0030] As for the time amount of vacuum evaporatio processing, it is desirable from the stability of quality that 120 or less minutes takes 10 minutes or more more preferably 480 or less minutes 10 minutes or more in industrial manufacture. The rate of flow of the inert gas containing the hydrocarbon at the time of vacuum evaporatio processing has 200 or less desirable cm/s more than per cm/s. Although vacuum evaporatio processing can be manufactured even in the moving beds, such as the fixed bed or a rotary furnace, it is desirable from processing temperature being made as for the approach of manufacturing with the fluid bed to homogeneity. Although the gas at the time of vacuum evaporatio processing can also be circulated, the approach of circulating, after a filter etc. removes the minute carbon particle which deposited is desirable.

[0031] After such vacuum evaporatio processing can obtain molecular sieve carbon by cooling under an inert gas ambient atmosphere.

[0032] By the above art, the pyrolytic carbon emitted from aromatic hydrocarbon or alicyclic hydrocarbon vapor-deposits near the micropore inlet port of a carbonaceous base material, and it has about 3-4A micropore by controlling appropriately the concentration of processing temperature, the processing time, aromatic hydrocarbon, or alicyclic hydrocarbon in the above-mentioned range, and repeatability is good and the narrow molecular sieve carbon of MIROKU pore size distribution can be manufactured cheaply.

[0033] In addition, after vacuum evaporatio processing, succeedingly, under an inert gas ambient atmosphere, if it holds in temperature of 1100 degrees C or less beyond vacuum evaporatio processing temperature, a still much more good result will be obtained. This effectiveness is in fixing firmly the diameter distribution of micropore acquired by vacuum evaporatio processing. Moreover, since there is effectiveness which narrows the path of the micropore exceeding 4A in elevated-temperature maintenance, there is effectiveness which makes Sharp more diameter distribution of micropore generated by vacuum evaporatio processing. This effectiveness is not acquired under at vacuum evaporatio processing temperature. Moreover, if temperature exceeds 1100 degrees C, since micropore will disappear rapidly, it is not desirable. By the approach explained above, the diameter of micropore can manufacture about 3-4A and narrow molecular sieve carbon with repeatability that it is simple, cheaply, and sufficient.

[0034]

[Example] Hereafter, an example explains this invention.

(Example 1) The coal-tar pitch was heat-treated and 210 degrees C of softening temperatures and the optical-isotropy pitch of 350 ppm or less of ash content were obtained. Extrusion spinning of this pitch was carried out, and pitch fiber with a diameter of 14 micrometers was obtained. All over the furnace, sending in air, the temperature up was carried out over 5 hours from a room temperature to 300 degrees C, and this pitch fiber was held for further 1 hour, and was made into pitch non-deliquescent fiber. The impeller mill (INP250 mold, Seishin Enterprise make) ground this pitch non-deliquescent fiber, and it considered as pitch non-deliquescent fiber of 0.35mm of mean fiber length. Next, the coal-tar pitch of 110 degrees C of softening temperatures was mixed at a rate of 15 weight sections to this grinding pitch non-deliquescent fiber 100 weight section. Rolling granulation of this mixed raw material was carried out adding water by the tumbling disk granulator of 1000mmphi, and the granulated body of the diameter of 3.35-4.8mm was obtained. This granulated body was dried at 200 degrees C, and moisture was removed. Hereafter, this granulated body will be called a fiber granulated body. This fiber granulated body was classified and it classified to the grain size of 3.35-4mm, and two 4-4.8mm kinds.

[0035] The fiber granulated body with a grain size of 3.35-4mm was heated to 300 degrees C all over the furnace, sending in nitrogen gas, after having heated to 1000 degrees C with 5-degree-C programming rate for /, holding at this temperature for 2 hours and performing activation processing, sending in the nitrogen gas which contains carbon dioxide gas 50% succeedingly, it cooled in nitrogen gas and the carbonaceous base material I was obtained. The activation yield of the carbonaceous base material I was 56%. The micropore was within the limits of 5-11A, as shown in drawing 1, the diameter of average micropore was 7.2A, and specific surface area was 800m<sup>2</sup> / g.

[0036] In addition, the diameter distribution of micropore is displayed due to the addition micropore volume and the diameter of micropore. micropore volume of 6A or less -- the adsorption isotherm of a carbon tetrachloride (6A of diameters of the minimum molecule), an isobutane (said -- 5.0A), n-butane (said -- 4.3A), ethane (said -- 4.0A), and carbon dioxide gas (said -- 3.3A) -- measuring -- a Dubinin-Astakhov plot to each maximum adsorption volume W<sub>0</sub> It asked and was made to represent with the value. Moreover, the larger micropore volume of a path than 6A analyzed and asked for the adsorption isotherm of the nitrogen in liquid nitrogen temperature by the MP method.

$W/W_0 = \exp \{ -(A/E)^n \}$

W : phase counter pressure -- P/P<sub>0</sub> it is -- the time -- filling -- having -- \*\*\*\* -- micropore -- the volume -- [-- cm<sup>3</sup>/g]

W<sub>0</sub> : The maximum adsorption volume [cm<sup>3</sup>/g]

A : adsorption potential [mol/joul]

E Property energy of :adsorption [joul/mol]

n : constant P<sub>0</sub> of 1-6 : Maximum vapor tension of the adsorption gas in measurement temperature [torr]

P : vapor pressure of adsorption gas [torr]

[0037] Next, the carbonaceous base material I was heated to 725 degrees C, sending in nitrogen gas all over a furnace. After holding for 90 minutes and performing pyrolytic carbon vacuum evaporatio processing, sending in the nitrogen gas which contains benzene 7.8% at this temperature succeedingly, it cooled with nitrogen gas and molecular sieve carbon I-1 was made as an experiment.

[0038] Similarly, the molecular sieve carbon I-2 which made 120 minutes the pyrolytic carbon vacuum evaporatio processing time using the carbonaceous base material I was made as an experiment. The diameter distribution of micropore of I-1 and I-2 is shown in drawing 1. Pyrolytic carbon vacuum evaporatio processing shows that micropore is narrow in about 3-4A, without reducing most micropore volume. next, in order to evaluate molecular sieve nature, the adsorption isotherm to the oxygen (2.8A of diameters of the minimum molecule) of I-1 and I-2, nitrogen (said -- 3.0A), carbon dioxide gas (said -- 3.3A), and methane (said -- 4.0A) was measured. The adsorption isotherm measuring device bell soap 18 (a high-pressure measurement specification and Japanese Bell) by the setting-the volume method was used for measurement. The result is shown in drawing 2 and drawing 3. There is a big difference in the amount of adsorption of methane and carbon dioxide gas (drawing 2), and I-1 and I-2 show the outstanding molecular sieve nature of a balanced discrete type. Moreover, I-2 shows some balanced discrete-type molecular sieve nature also to oxygen and

nitrogen ( drawing 3 ). Drawing 4 measures the rate of adsorption of the nitrogen of I-1 and I-2, and oxygen. After the measuring method put in the molecular sieve carbon sample in the container of volume known and made the inside of a system the vacuum , it introduced the gas ( nitrogen , oxygen ) make to adsorb , depends it on the approach of measure the time amount and the pressure after installation , and was enforced using the bell soap 18 same as equipment as measurement of adsorption isotherm . The time amount which the completion of adsorption of nitrogen takes from drawing 4 to adsorption completing oxygen within very short time amount understands a \*\*\*\*\* very much. That is, it is clear 2 [ I-1 and / I-] to have the molecular sieve nature of a very good rate discrete type.

[0039] (Example 2) Activation of the fiber granulated body with a grain size of 3.35-4mm manufactured in the example 1 was carried out by the same approach as an example 1, and the carbonaceous base material G was obtained. However, the holding time in 1000 degrees C was made into 1 hour. The activation yield of the carbonaceous base material G was 65%. The micropore was within the limits of 5-10A, as shown in drawing 5 , the diameter of average micropore was 6.2A, and specific surface area was 590m<sup>2</sup> / g.

[0040] Next, the carbonaceous base material G was heated to 725 degrees C, sending in nitrogen gas all over a furnace. It held for 60 minutes at 750 degrees C, sending in nitrogen gas further, after holding benzene at this temperature for 60 minutes, sending in 7.8% or the nitrogen gas included 12.6% and performing pyrolytic carbon vacuum evaporatono processing succeedingly, and cooled with nitrogen gas after that, and two kinds of molecular sieve carbon G-1 (benzene: 7.8%) and G-2 (benzene: 12.6%) were made as an experiment.

[0041] The diameter distribution of micropore of G-1 and G-2 is shown in drawing 5 . Pyrolytic carbon vacuum evaporatono processing shows that micropore is narrow in 3-4A, without reducing the micropore volume.

[0042] Next, in order to evaluate molecular sieve nature, the adsorption isotherm of carbon dioxide gas, methane, oxygen, and nitrogen was measured. The result is shown in drawing 6 and drawing 7 . This drawing 6 shows having the balanced discrete-type molecular sieve engine performance in which G-1 and G-2 were excellent to methane and carbon dioxide gas. Moreover, drawing 7 shows that G-2 has the balanced discrete-type molecular sieve engine performance also to oxygen and nitrogen.

[0043] Drawing 8 is the result of measuring the rate of adsorption of the nitrogen of G-1 and G-2, and oxygen. This drawing shows having the rate discrete-type molecular sieve engine performance in which G-1 and G-2 were excellent to nitrogen and oxygen.

[0044] (Example 3) Activation of the fiber granulated body with a grain size of 4-4.8mm manufactured in the example 1 was carried out by the same approach as an example 2, and the carbonaceous base material H was obtained. The activation yield of the carbonaceous base material H was 69%. The micropore was within the limits of 5-9A, as shown in drawing 9 , the diameter of average micropore was 6.0A, and specific surface area was 470m<sup>2</sup> / g.

[0045] Next, the carbonaceous base material H was heated to 725 degrees C, sending in nitrogen gas all over a furnace. After holding for 90 minutes and performing pyrolytic carbon vacuum evaporatono processing, sending in the nitrogen gas which contains benzene 7.8% at this temperature succeedingly, it cooled with nitrogen gas and molecular sieve carbon H-1 was made as an experiment.

[0046] The diameter distribution of micropore of H-1 is shown in drawing 9 . Pyrolytic carbon vacuum evaporatono processing shows that micropore is narrow in 3-4A, without reducing the micropore volume.

[0047] Next, in order to evaluate molecular sieve nature, the adsorption isotherm of carbon dioxide gas, methane, oxygen, and nitrogen was measured. The result is shown in drawing 10 and drawing 11 . Drawing 10 and drawing 11 show that H-1 has the balanced discrete-type molecular sieve engine performance in which it excelled also to oxygen and nitrogen, as opposed to methane and carbon dioxide gas.

[0048] Drawing 12 is the result of measuring the rate of adsorption of the nitrogen of H-1, and oxygen. This drawing shows that H-1 has the rate discrete-type molecular sieve engine performance in which it excelled not only in the balanced discrete type, to nitrogen and oxygen.



[0049]

[Effect of the Invention] According to the manufacturing method of the molecular sieve carbon of this invention, it is about 3-4A of diameters of micropore, and repeatability is good simple and the narrow molecular sieve carbon of the diameter distribution of micropore can be manufactured. Especially the molecular sieve carbon obtained by this invention is excellent in the rate discrete-type molecular sieve engine performance to methane, the balanced discrete-type molecular sieve engine performance to carbon dioxide gas and nitrogen, and oxygen.

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[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] They are the carbonaceous base material I and molecular sieve carbon I-1, and drawing that expressed the diameter distribution of micropore of I-2 by cumulative size distribution. The axis of abscissa of an axis of ordinate is a diameter of micropore about the micropore volume of addition.

[Drawing 2] molecular sieve carbon I-1 and I-2 -- they are each carbon dioxide gas and drawing showing the adsorption isotherm of methane.

[Drawing 3] It is drawing showing the adsorption isotherm of molecular sieve carbon I-1 and the nitrogen of I-2, and oxygen.

[Drawing 4] It is drawing which expressed the rate of adsorption of the nitrogen of molecular sieve carbon I-1, and oxygen by change of the amount of adsorption to time amount.

[Drawing 5] They are the carbonaceous base material G and molecular sieve carbon G-1, and drawing that expressed the diameter distribution of micropore of G-2 by cumulative size distribution.

[Drawing 6] It is drawing showing molecular sieve carbon G-1, the carbon dioxide gas of G-2, and the adsorption isotherm of methane.

[Drawing 7] It is drawing showing the adsorption isotherm of molecular sieve carbon G-1, the nitrogen of G-2, and oxygen.

[Drawing 8] It is drawing which expressed the rate of adsorption of molecular sieve carbon G-1, the nitrogen of G-2, and oxygen by change of the amount of adsorption to time amount.

[Drawing 9] It is drawing which expressed the diameter distribution of micropore of the carbonaceous base material H and molecular sieve carbon H-1 by cumulative size distribution.

[Drawing 10] It is drawing showing the carbon dioxide gas of molecular sieve carbon H-1, and the adsorption isotherm of methane.

[Drawing 11] It is drawing showing the adsorption isotherm of the nitrogen of molecular sieve carbon H-1, and oxygen.

[Drawing 12] It is drawing which expressed the rate of adsorption of the nitrogen of molecular sieve carbon H-1, and oxygen by change of the amount of adsorption to time amount.

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[Translation done.]

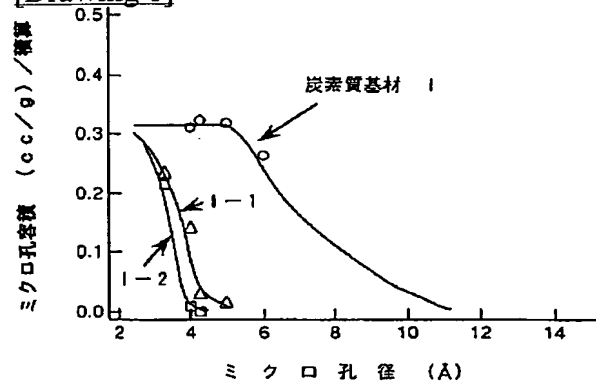
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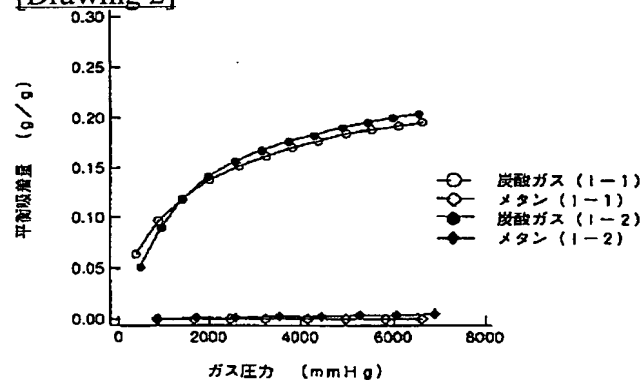
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## DRAWINGS

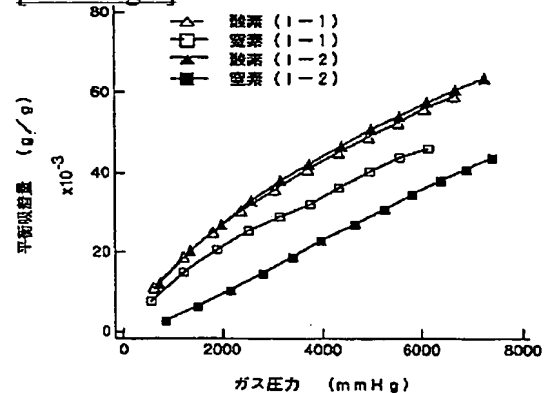
[Drawing 1]



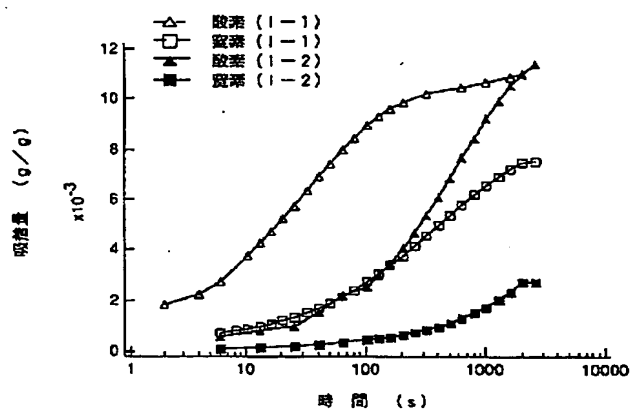
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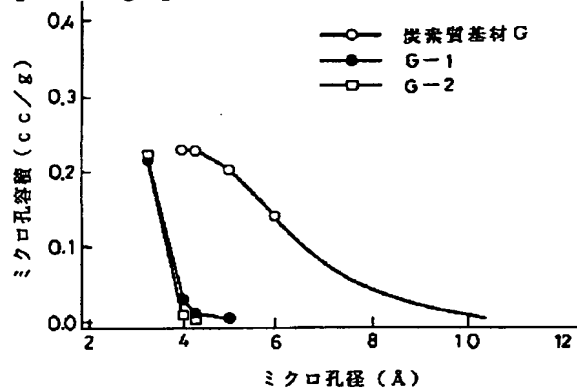
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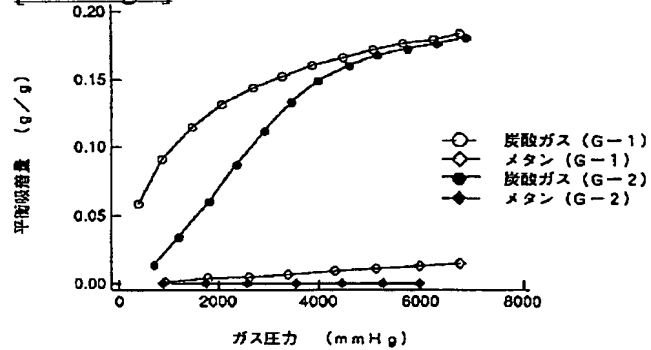
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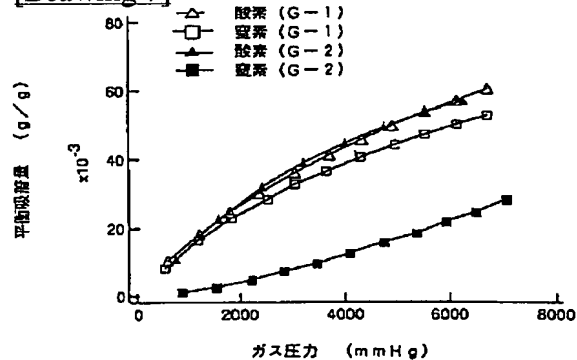
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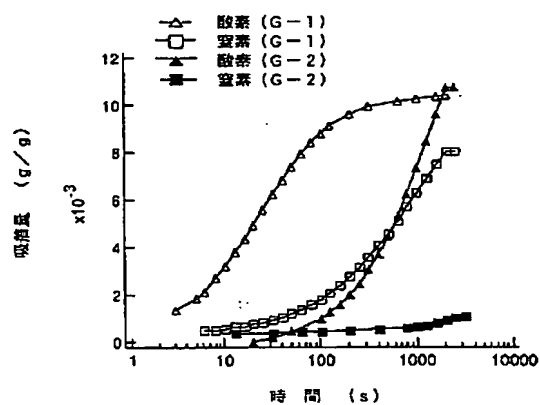
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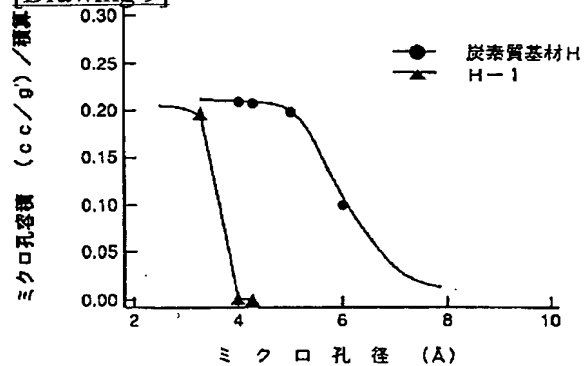
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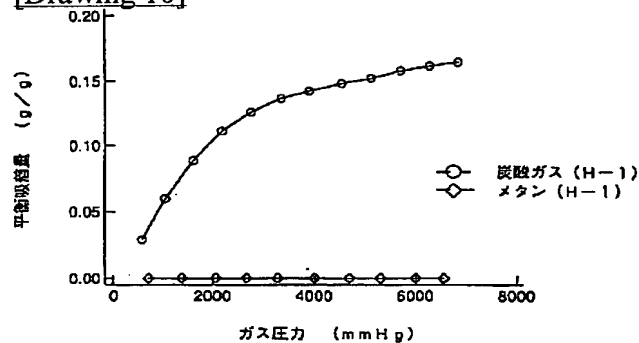
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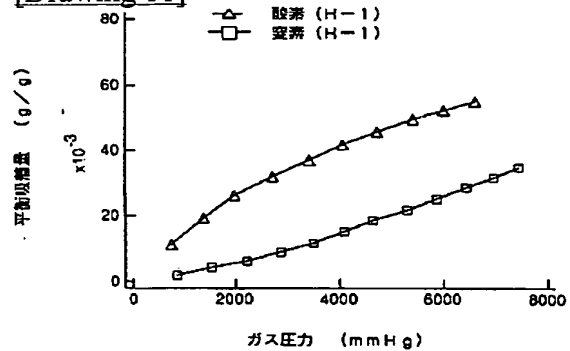
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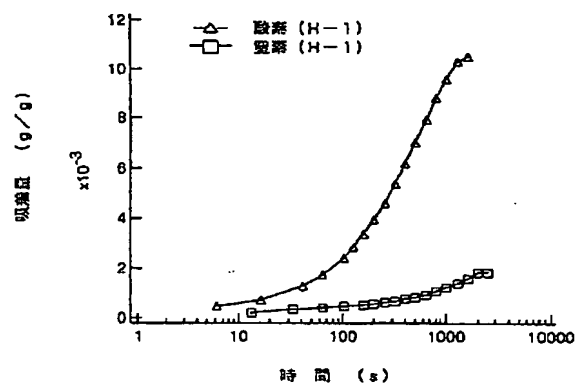
[Drawing 10]



[Drawing 11]



[Drawing 12]



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[Translation done.]

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最終頁に続く

(54)【発明の名称】 分子ふるい炭素の製造方法

(57)【要約】

【構成】不活性ガス雰囲気下で650～850℃に加熱され、5.5～12Åの平均マイクロ孔径を有する炭素質基材を、650～850℃に加熱された処理炉中で、該反応炉に芳香族炭化水素または脂環式炭化水素を含む不活性ガスを供給して蒸着処理することを特徴とする分子ふるい炭素の製造方法。

【効果】本発明の分子ふるい炭素の製造法によれば、マイクロ孔径3～4Å強でかつ、マイクロ孔径分布の狭い分子ふるい炭素を、簡便にかつ再現性良く、製造することができる。本発明によって得られる分子ふるい炭素は、特に、メタン、炭酸ガスに対する平衡分離型分子ふるい性能、ならびに窒素、酸素に対する速度分離型分子ふるい性能に優れている。

## 【特許請求の範囲】

【請求項1】5.5～12Åの平均マイクロ孔径を有する炭素質基材を、650～850℃に加熱した処理炉中で、芳香族炭化水素および／または脂環式炭化水素を含む不活性ガスを供給して熱分解炭素をマイクロ孔に蒸着することを特徴とする分子ふるい炭素の製造方法。

【請求項2】不活性ガス雰囲気下で650～850℃に加熱され、5.5～12Åの平均マイクロ孔径を有する炭素質基材を、650～850℃に加熱された処理炉中で、該反応炉に芳香族炭化水素および／または脂環式炭化水素を含む不活性ガスを供給して蒸着処理することを特徴とする分子ふるい炭素の製造方法。

【請求項3】前記炭素質基材が、軟化点150℃以上、灰分5000ppm以下の光学的等方性ビッチを原料として製造されたものであることを特徴とする請求項1または2に記載の分子ふるい炭素の製造方法。

【請求項4】軟化点150℃以上、灰分5000ppm以下の光学的等方性ビッチを、粉砕ないしは繊維とし、これを不融化し、次いで成型し、さらに炭酸ガスおよび／または水蒸気を含む不活性ガス雰囲気下で賦活処理を施して比表面積300～1000m<sup>2</sup>/gの多孔性炭素とし、これを前記炭素質基材として使用する請求項1～3いずれかに記載の分子ふるい炭素の製造方法。

【請求項5】前記蒸着処理終了後、引き続き不活性ガス雰囲気下に蒸着処理温度以上1100℃以下の温度で保持することを特徴とする請求項1～4いずれかに記載の分子ふるい炭素の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、PSA手法による空気分離、オフガス等からの水素精製、発酵ガス中からのメタンの分離等、ガス分離技術に用いられる分子ふるい炭素の製造方法に関するものである。

## 【0002】

【従来の技術】近年、各種混合ガス中から特定の成分を分離、精製する技術開発が盛んである。中でもPSAと称される手法は、装置がコンパクトでランニングコストが低いため、多くの用途への展開が期待されている。特に、疎水性の分子ふるい炭素を用いて、空気から窒素を分離、回収する空気分離は、窒素需要の増大に伴って、急激な市場拡大が見込まれる。分子ふるい炭素の特徴は、通常の活性炭が10～30Åのマイクロ孔を持つのに対し、3～5Åという小さく、かつ狭い分布のマイクロ孔を持っていることにある。分子ふるい炭素の製造方法に関しては、種々の方法が提案されているが、その中に熱分解炭素蒸着法がある。

【0003】この熱分解炭素蒸着法は、炭素質基材と炭化水素ガスを高温で接触させ、炭化水素から放出される熱分解炭素を炭素質基材のマイクロ孔の入り口付近に蒸着させることで、炭素質基材のマイクロ孔を調節する方法で

あり、従来よりこの方法に関する各種の提案がある。

【0004】特公昭52-18675号明細書に於いては、揮発性成分の少ないコークスを炭素質基材として用い、熱分解により炭素を放出する炭化水素（例えばベンゼン、トルエン、エタン、ヘキサン、メタノールなど）を添加して600～900℃の温度で1～60分間またはそれ以上の時間処理することによって、放出された炭素を該コースの細孔中に沈着させることにより、約4Å以下の小さい分子寸法をもつガスの分離に使用される炭素含有分子ふるいの製法が提案されている。

【0005】この提案は、小さい分子を分離するための炭素分子ふるいの製法を始めて提案した点で画期的であり評価されるが、再現性良く優れた高品質の炭素分子ふるいを得るためにさらなる改善が必要である。

【0006】また、特表平1-502743号明細書に於いては、揮発性成分の少ない乾留物を800～900℃の温度で、5～30分間、向流で20～95容量%の水蒸気濃度を有する不活性ガスが供給される振動炉中に導入して、弱く活性化を施した後、向流で5～12容量%のベンゼン濃度を有する不活性ガスが供給される振動炉に導入することにより、酸素および窒素の分離能に優れ、均一な品質を有する分子ふるいの製造方法を開示している。

【0007】この提案はより均一な品質の製品が得られる点に於いて優れるが、向流で接触する方式であるため、若干プロセスが複雑になり、また、使用する乾留物によっては高品質のものが得られない場合がある。

【0008】別の提案として、特開昭60-171212号明細書に於いて、(i)高温(800～900℃)で炭素基材を脱ガスする工程、(ii)脱ガス後の炭素基材を300～500℃の温度まで冷却し、気相の炭化水素と接触させて、この炭化水素を内部に吸着させる工程、(iii)吸着後の炭素基材を減圧下に脱ガスして物理的に保持された炭化水素を除去する工程および(iv)炭素基材の細孔に固着した炭化水素を高温(800～900℃)で分解して細孔に炭素を沈着させる工程、以上(i)～(iv)の工程の組合わせからなる分子ふるい炭素の製法が提案されており、炭素基材に吸着される炭化水素としてプロピレンを用いた場合について開示を行い、プロピレンの最低寸法から、0.5～0.55nm(5～5.5Å)の細孔を有する炭素基材の処理に最も適しているとしている。

【0009】この提案によれば炭素基材の開口部のみに熱分解炭素が沈着し、細孔構造が制御された分子ふるい炭素を製造することができるが、全体として製造工程は複雑かつ煩雑となる。

## 【0010】

【発明が解決しようとする課題】本発明は、このような熱分解炭素蒸着法による分子ふるい炭素の改善された製造方法の提供を目的とする。より具体的には、高性能の



分子ふるい炭素を簡便に、安価に、再現性良く製造する方法の提供を目的とする。

【0011】

【課題を解決するための手段】本発明者らは、ピッチを出発原料として炭素質基材のミクロ孔径と熱分解炭素の発生源である炭化水素の種類との関係につき鋭意研究を行った処、平均ミクロ孔径が5.5～12Åの炭素質基材を用い、炭化水素として芳香族炭化水素、または脂環式炭化水素を用いると極めて簡便なプロセスで高性能の分子ふるい炭素を再現性良く製造することができることを見出し、本発明を完成するに至った。

【0012】すなわち、本発明の包括的概念によれば、5.5～12Åの平均ミクロ孔径を有する炭素質基材を、650～850℃に加熱した処理炉中で、芳香族炭化水素および／または脂環式炭化水素を含む不活性ガスを供給して熱分解炭素をミクロ孔に蒸着することを特徴とする分子ふるい炭素の製造方法が提供される。

【0013】また、不活性ガス雰囲気下で650～850℃に加熱され、5.5～12Åの平均ミクロ孔径を有する炭素質基材を、650～850℃に加熱された処理炉中で、該反応炉に芳香族炭化水素および／または脂環式炭化水素を含む不活性ガスを供給して蒸着処理することと特徴とする分子ふるい炭素の製造方法が提供される。

【0014】ここで、前記炭素質基材が、軟化点150℃以上、灰分5000ppm以下の光学的等方性ピッチを原料として製造され、軟化点150℃以上、灰分5000ppm以下の光学的等方性ピッチを、粉碎ないしは繊維とし、これを不融化し、次いで成型し、さらに炭酸ガスおよび／または水蒸気を含む不活性ガス雰囲気下で賦活処理を施して比表面積300～1000m<sup>2</sup>/gの多孔性炭素とし、これを前記炭素質基材として使用するのが好ましい。

【0015】さらに、前記蒸着処理終了後、引き続き不活性ガス雰囲気下に蒸着処理温度以上1100℃以下の温度で保持するのが好ましい。

【0016】

【構成】以下、本発明の構成を詳述するが、より好ましい態様およびそれに基づく利点が自ずと明らかになる。

【0017】炭素質基材

本発明で使用する炭素質基材の平均ミクロ孔径は5.5～12Åの範囲であり、好ましくは5.5～9Å、特に5.5～8Åである。炭素質基材のミクロ孔径の分布が狭いと得られる分子ふるい炭素のミクロ孔径の分布も狭くなり、好適な結果を得る。平均ミクロ孔径が5.5Å未満の炭素質基材の場合、芳香族炭化水素の熱分解により発生した炭素で蒸着処理する際に、ミクロ孔径が狭くなる速度（ミクロ孔径の経時変化）が早すぎるため、ミクロ孔径の制御が困難となり適切でない。また、平

均径が12Åを越えると蒸着処理の際にミクロ孔自体が閉塞されやすくなるので適切でない。

【0018】なお、本発明におけるミクロ孔とは、20Å以下の細孔を示す。また、平均ミクロ孔径とはミクロ孔径の分布曲線に於いてミクロ孔容積の50%平均径を意味する。5.5～12Åの範囲内の平均ミクロ孔径を有する炭素質基材は、石炭系または石油系のピッチを出発原料として以下に詳述する方法に従い極めて容易に得ることができる。

10 【0019】以下、炭素質基材の取得方法について述べる。軟化点が150℃以上、好ましくは150～250℃で、灰分が5000ppm以下、好ましくは500ppm以下の、光学的に等方性のピッチを機械的に粉碎して微粉状とする。または光学的に等方性のピッチを加熱して、熔融紡糸の手法で繊維状とする。

【0020】軟化点が150℃以下のピッチは、不融化に多大の時間を要するため、出発原料としては適切でない。また、灰分が5000ppm以上のピッチは、灰分が触媒として作用するため、後述する賦活反応を暴走させる、あるいは得られる炭素質基材の平均ミクロ孔径が12Åを超えやすい、等の点から出発原料として適切でない。この微粉状ピッチあるいは繊維状ピッチを空気等の酸性雰囲気下で300℃まで昇温して不融化する。

【0021】不融化した微粉状物あるいは繊維状物はバインダーと混合して、成型する。ここでバインダーとは微粉状物あるいは繊維状物同士を結合せしめ成型された形状を保持する機能を有するものであり、軟化点が80～120℃程度のピッチ、フェノール樹脂、フuran樹脂、エポキシ樹脂などを例示できる。バインダーの使用割合は残留炭素分として不融化した微粉状物および繊維状物100重量部に対して2重量部以上30重量部以下が好ましい。30重量部より大きいと、賦活処理が容易ではなくなり、細孔分布が広がり分子ふるい炭素の原料として好ましくなくなる。2重量部未満の場合前記のバインダーとしての効果が発現しない。

【0022】この成型工程により、微粉状の不融化物は押出造粒法あるいは転動造粒法により粒状に成型される。繊維状の不融化物は微粉状の場合と同様に粒状に成型され、またその他湿式抄紙法によるペーパーやニードルパンチ法によるフェルト等に成型される。

【0023】この成型品は次に賦活処理に付される。賦活処理においては、炭材（賦活原料）を構成する炭素結晶体、あるいは微細な孔隙部分を構成する炭素が反応消耗して、炭素構造により孔隙が複雑に組織的に形成し、比表面積が増大する。

【0024】賦活処理は、炭酸ガス雰囲気下あるいは炭酸ガスまたは／および水蒸気を含む窒素ガスなどの不活性ガス雰囲気下で800～1100℃の温度で、0～480分放置することにより行われる。賦活処理前にか

50 じめ窒素ガスなどの不活性ガス雰囲気中で500～1

500℃の温度で炭化処理してもよい。

【0025】この賦活処理で、処理物の比表面積が300～1000m<sup>2</sup>/gとなるように処理温度と時間を制御することにより、平均ミクロ孔径が5.5～12Åの範囲内にある炭素質基材を容易に製造することができる。この程度の賦活化であれば、賦活収率（微粉状物あるいは繊維状物の成型物重量に対する賦活処理物重量の割合）は50～70%と高く分子ふるい炭素を安価に得ることができる。

#### 【0026】炭化水素

本発明の熱分解炭素蒸着法の炭素源となる炭化水素として、芳香族炭化水素もしくは、脂環式炭化水素が用いられる。芳香族炭化水素としては、ベンゼン、トルエン、エチルベンゼン、キシレンなどのアルキルベンゼン、その他ナフタレン、メチルナフタレンなど、また脂環式炭化水素としてはシクロヘキサンなどを例示できるが、一般的には炭素環が1～2環程度のものが好ましい。

#### 【0027】蒸着処理法

本発明に於いては、まず前述の炭素質基材を不活性ガス雰囲気下で650～850℃好ましくは700～800℃まで加熱される。この加熱は後述する処理炉中で行ってもよいし、別の炉中で加熱し、加熱された炭素質基材を連続的に処理炉に供給してもよい。

【0028】蒸着処理は650～850℃、好ましくは700～750℃に加熱された処理炉中で行われる。処理炉中には前記の加熱された炭素質基材が存在し、そこへ芳香族炭化水素、または脂環式炭化水素を0.1～20容量%、好ましくは3～10容量%含有する窒素ガスで代表される不活性ガスが供給される。

【0029】なお、処理炉の温度が650℃未満では熱分解炭素の発生量が少なく、蒸着に膨大な時間を要し、850℃を超える温度では熱分解炭素の発生量が多すぎて、ミクロ孔径が狭くなる速度が速くなり制御不能となる。

【0030】蒸着処理の時間は、工業的な製造では10分以上480分以下、より好ましくは10分以上120分以下とするのが品質の安定性から好ましい。蒸着処理時の炭化水素を含有する不活性ガスの流速は、1cm/s以上200cm/s以下が好ましい。蒸着処理は固定床でも回転炉などの移動床でも製造可能であるが、流動床で製造する方法が処理温度を均一にできることから好ましい。蒸着処理時のガスは循環させることもできるが、析出した微小炭素粒子をフィルターなどで除去した後循環する方法が好ましい。

【0031】このような蒸着処理後は、不活性ガス雰囲気下で冷却することにより分子ふるい炭素を得ることができる。

【0032】以上の処理方法により、芳香族炭化水素または脂環式炭化水素から放出される熱分解炭素が炭素質基材のミクロ孔入口付近に蒸着し、処理温度、処理時

間、芳香族炭化水素または脂環式炭化水素の濃度を前述の範囲で適切に制御することにより3～4Å強のミクロ孔を持ち、かつミクロ孔径分布の狭い分子ふるい炭素を再現性良く、安価に製造することができる。

【0033】なお、蒸着処理後、引き続き不活性ガス雰囲気下で蒸着処理温度以上、1100℃以下の温度に保持すると、なお一層良い結果を得る。この効果は、蒸着処理で得られたミクロ孔径分布を強固に固定することにある。また、高温保持には4Åを超えるミクロ孔の径を狭める効果もあるので、蒸着処理で生成したミクロ孔径分布をよりシャープにする効果もある。蒸着処理温度未満ではこの効果は得られない。また、温度が1100℃を超えると、ミクロ孔が急激に消失するので好ましくない。以上に説明した方法により、ミクロ孔径が3～4Å強と狭い分子ふるい炭素を簡便に、安価に、かつ再現性良く製造することができる。

#### 【0034】

【実施例】以下、本発明を実施例により説明する。

（実施例1）コールタールピッチを熱処理して、軟化点210℃、灰分350ppm以下の光学的等方性ピッチを得た。このピッチを押出紡糸し、直径14μmのピッチ繊維を得た。このピッチ繊維を炉中で、空気を送り込みながら、室温から300℃まで5時間かけて昇温し、さらに1時間保持してピッチ不融化繊維とした。このピッチ不融化繊維をインペラーミル（INP250型、セイシン企業（株）製）で粉碎し、平均繊維長0.35mmのピッチ不融化繊維とした。次に、この粉碎ピッチ不融化繊維100重量部に対し、軟化点110℃のコールタールピッチを15重量部の割合で混合した。この混合原料を1000mmφの皿型造粒機で水を添加しながら転動造粒し、3.35～4.8mm径の造粒体を得た。この造粒体を200℃で乾燥して水分を除去した。以下、この造粒体を繊維造粒体と呼ぶことにする。この繊維造粒体を分級して、粒度3.35～4mmと4～4.8mmの2種類に分別した。

【0035】粒度3.35～4mmの繊維造粒体を炉中で、窒素ガスを送り込みながら300℃まで加熱し、引き続き炭酸ガスを50%含む窒素ガスを送り込みながら、5℃/分の昇温速度で1000℃まで加熱し、この温度で2時間保持して賦活処理を施した後、窒素ガス中で冷却して炭素質基材1を得た。炭素質基材1の賦活収率は56%であった。そのミクロ孔は、図1に示すように、5～11Åの範囲内にあり、平均ミクロ孔径は7.2Åで、比表面積は800m<sup>2</sup>/gであった。

【0036】なお、ミクロ孔径分布は、積算ミクロ孔容積とミクロ孔径の関係で表示してある。6Å以下のミクロ孔容積は、四塩化炭素（最小分子径6Å）、イソブタン（同5.0Å）、n-ブタン（同4.3Å）、エタン（同4.0Å）、炭酸ガス（同3.3Å）の吸着等温線を測定し、Dubinin-Astakhovプロットから、各々の最大

吸着容積 $W$ を求め、その値で代表させた。また、6 Åより大きい径のミクロ孔容積は、液体窒素温度における窒素の吸着等温線をMP法で解析して求めた。

$$W/W_0 = \exp \{ - (A/E)^n \}$$

$W$  : 相対圧が $P/P_0$ のとき満されているミクロ孔容積 [ $\text{cm}^3/\text{g}$ ]

$W_0$  : 最大吸着容積 [ $\text{cm}^3/\text{g}$ ]

$A$  : 吸着ポテンシャル [ $\text{mol}/\text{jou}$ ]

$E$  : 吸着の特性エネルギー [ $\text{jou}/\text{mol}$ ]

$n$  : 1~6の定数

$P_0$  : 測定温度における吸着ガスの飽和蒸気圧 [torr]

$P$  : 吸着ガスの蒸気圧 [torr]

【0037】次に、炭素質基材Iを炉中で窒素ガスを送り込みながら、725℃まで加熱した。引き続きこの温度でベンゼンを7.8%含む窒素ガスを送り込みながら、90分保持して熱分解炭素蒸着処理を施した後、窒素ガスで冷却し、分子ふるい炭素I-1を試作した。

【0038】同様に、炭素質基材Iを用いて熱分解炭素蒸着処理時間を120分とした分子ふるい炭素I-2を試作した。図1に、I-1およびI-2のミクロ孔径分布を示す。熱分解炭素蒸着処理により、ミクロ孔容積をほとんど減ずることなく、ミクロ孔が3~4 Å強に狭まっていることがわかる。次に分子ふるい性を評価するため、I-1およびI-2の酸素（最小分子径2.8 Å）、窒素（同3.0 Å）、炭酸ガス（同3.3 Å）、メタン（同4.0 Å）に対する吸着等温線を測定した。測定には、定容法による吸着等温線測定装置ベルソーブ18（高圧測定仕様、日本ベル（株））を用いた。その結果を、図2、図3に示す。I-1およびI-2とも、メタンと炭酸ガスの吸着量には大きな差があり（図2）、優れた平衡分離型の分子ふるい性を示している。また、I-2は、酸素、窒素に対しても多少の平衡分離型分子ふるい性を示している（図3）。図4は、I-1、I-2の窒素、酸素の吸着速度を比較したものである。測定方法は容積既知の容器内に分子ふるい炭素サンプルを入れ、系内を真空にした後、吸着させるガス（窒素、酸素）を導入し、導入後の時間と圧力を計測する方法によるもので、装置としては吸着等温線の測定と同じベルソーブ18を用いて実施した。図4から、酸素は非常に短い時間内で吸着が完了するのに対し、窒素の吸着完了に要する時間は非常に長いことがわかる。つまり、I-1、I-2は非常に良好な速度分離型の分子ふるい性を持つことが明らかである。

【0039】（実施例2）実施例1で製造した粒度3.35~4 mmの繊維造粒体を、実施例1と同じ方法で賦活して、炭素質基材Gを得た。ただし、1000℃における保持時間は、1時間とした。炭素質基材Gの賦活収率は65%であった。そのミクロ孔は、図5に示すように、5~10 Åの範囲内にあり、平均ミクロ孔径は6.2 Åで、比表面積は590  $\text{m}^2/\text{g}$ であった。

【0040】次に、炭素質基材Gを、炉中で窒素ガスを送り込みながら725℃まで加熱した。引き続きこの温度でベンゼンを7.8%あるいは12.6%含む窒素ガスを送り込みながら、60分保持して熱分解炭素蒸着処理を施した後、さらに窒素ガスを送り込みながら750℃で60分間保持し、その後窒素ガスで冷却し、2種類の分子ふるい炭素G-1（ベンゼン：7.8%）、G-2（ベンゼン：12.6%）を試作した。

【0041】図5に、G-1およびG-2のミクロ孔径分布を示す。熱分解炭素蒸着処理により、ミクロ孔容積を減ずることなく、ミクロ孔が3~4 Åに狭まっていることがわかる。

【0042】次に、分子ふるい性を評価するため、炭酸ガス、メタン、酸素、窒素の吸着等温線を測定した。その結果を図6、図7に示す。この図6から、G-1、G-2ともメタン、炭酸ガスに対し、優れた平衡分離型分子ふるい性能を持っていることがわかる。また、図7から、G-2は酸素、窒素に対しても平衡分離型分子ふるい性能を持っていることがわかる。

【0043】図8は、G-1、G-2の窒素、酸素の吸着速度を比較した結果である。この図から、G-1、G-2とも窒素、酸素に対し、優れた速度分離型分子ふるい性能を持っていることがわかる。

【0044】（実施例3）実施例1で製造した粒度4~4.8 mmの繊維造粒体を、実施例2と同じ方法で賦活して、炭素質基材Hを得た。炭素質基材Hの賦活収率は69%であった。そのミクロ孔は、図9に示すように、5~9 Åの範囲内にあり、平均ミクロ孔径は6.0 Åで、比表面積は470  $\text{m}^2/\text{g}$ であった。

【0045】次に、炭素質基材Hを炉中で窒素ガスを送り込みながら、725℃まで加熱した。引き続きこの温度でベンゼンを7.8%含む窒素ガスを送り込みながら、90分保持して熱分解炭素蒸着処理を施した後、窒素ガスで冷却し、分子ふるい炭素H-1を試作した。

【0046】図9に、H-1のミクロ孔径分布を示す。熱分解炭素蒸着処理により、ミクロ孔容積を減ずることなく、ミクロ孔が3~4 Åに狭まっていることがわかる。

【0047】次に、分子ふるい性を評価するため、炭酸ガス、メタン、酸素、窒素の吸着等温線を測定した。その結果を図10、図11に示す。図10、図11から、H-1はメタン、炭酸ガスに対し、また酸素、窒素に対しても優れた平衡分離型分子ふるい性能を持っていることがわかる。

【0048】図12は、H-1の窒素、酸素の吸着速度を比較した結果である。この図から、H-1は窒素、酸素に対し平衡分離型だけでなく、優れた速度分離型分子ふるい性能を持っていることがわかる。

【0049】

【発明の効果】本発明の分子ふるい炭素の製造法によれ

ば、ミクロ孔径3~4 Å強で、かつ、ミクロ孔径分布の狭い分子ふるい炭素を、簡便にかつ再現性良く、製造することができる。本発明によって得られる分子ふるい炭素は、特に、メタン、炭酸ガスに対する平衡分離型分子ふるい性能、ならびに窒素、酸素に対する速度分離型分子ふるい性能に優れている。

【図面の簡単な説明】

【図1】 炭素質基材I、および分子ふるい炭素I-1、I-2のミクロ孔径分布を積算分布で表現した図である。縦軸は積算のミクロ孔容積を、横軸はミクロ孔径

【図2】 分子ふるい炭素I-1、I-2各々の炭酸ガス、メタンの吸着等温線を示す図である。

【図3】 分子ふるい炭素I-1およびI-2の窒素、酸素の吸着等温線を示す図である。

【図4】 分子ふるい炭素I-1の窒素と酸素の吸着速度を、時間に対する吸着量の変化で表現した図である。

【図5】 炭素質基材G、および分子ふるい炭素G-1、G-2のミクロ孔径分布を積算分布で表現した図である。

\* 1、G-2のミクロ孔径分布を積算分布で表現した図である。

【図6】 分子ふるい炭素G-1、G-2の炭酸ガス、メタンの吸着等温線を示す図である。

【図7】 分子ふるい炭素G-1、G-2の窒素、酸素の吸着等温線を示す図である。

【図8】 分子ふるい炭素G-1、G-2の窒素と酸素の吸着速度を、時間に対する吸着量の変化で表現した図である。

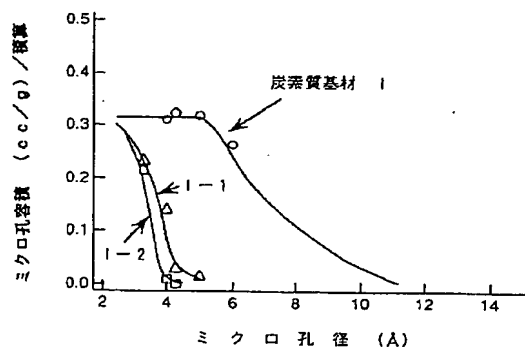
【図9】 炭素質基材H、および分子ふるい炭素H-1のミクロ孔径分布を積算分布で表現した図である。

【図10】 分子ふるい炭素H-1の炭酸ガス、メタンの吸着等温線を示す図である。

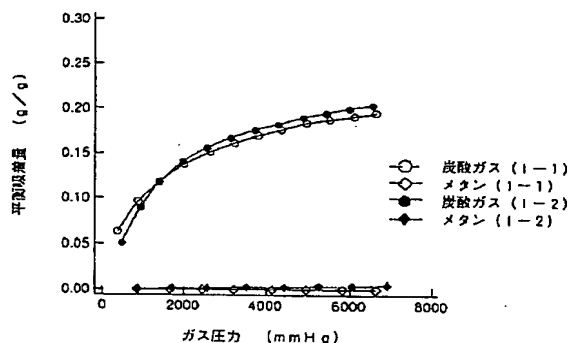
【図11】 分子ふるい炭素H-1の窒素、酸素の吸着等温線を示す図である。

【図12】 分子ふるい炭素H-1の窒素と酸素の吸着速度を、時間に対する吸着量の変化で表現した図である。

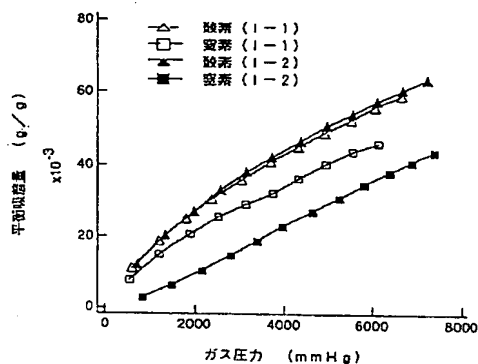
【図1】



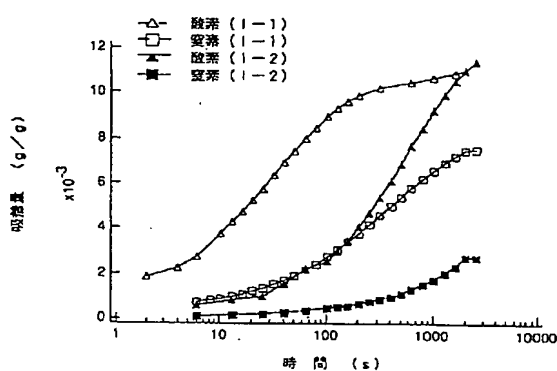
【図2】



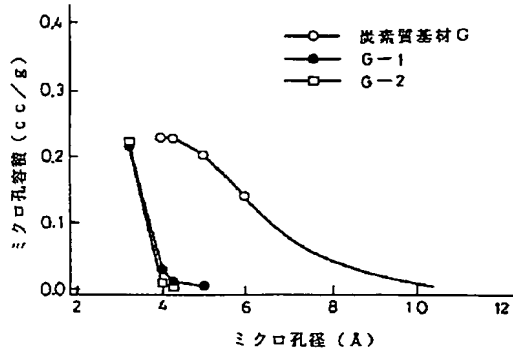
【図3】



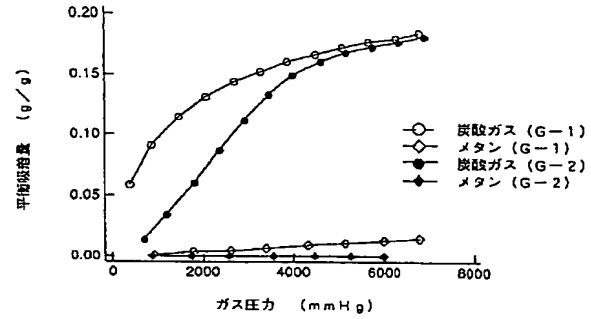
【図4】



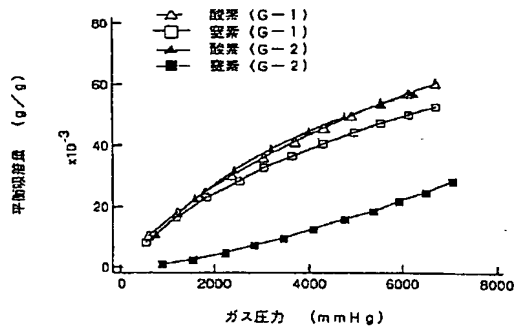
【図5】



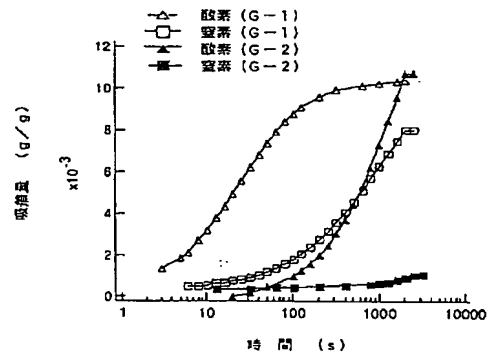
【図6】



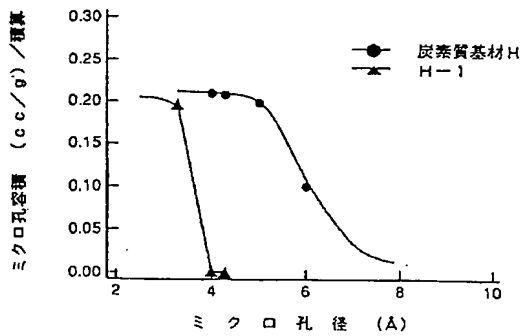
【図7】



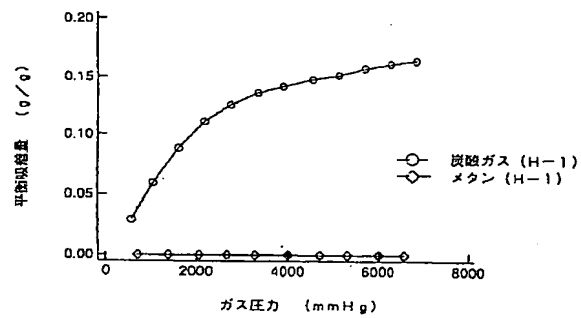
【図8】



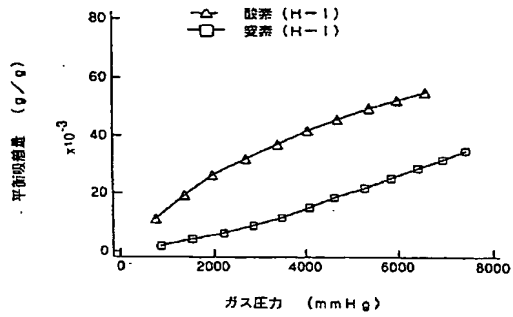
【図9】



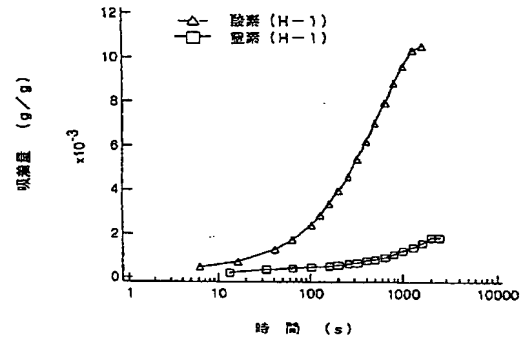
【図10】



【図11】



【図12】



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